REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	August 16, 1999	Technical Report # 49

4. TITLE AND SUBTITLE
Tunable Multicolor Electroluminescent Polymer Devices for Full Color Displays.

5. FUNDING NUMBERS
N00014-94-1-0540
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R & T Code 3132111

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8. PERFORMING ORGANIZATION REPORT NUMBER
49

9. SPONSORING / MONITORING AGENCY NAMES(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Published in POLYMER PREPRINTS, **1999**, *40 (2)*, 1194-1195.

a. DISTRIBUTION / AVAILABILITY STATEMENT
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12. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Efficient light emitting diodes (LEDs) of various colors and suitable methods of their pixelation are essential to incorporating polymer LEDs into full color display systems. We have developed polymer/polymer heterojunction LEDs that exhibit multicolor emmision which is tunable by the bias voltage. These LEDs are based on poly(p-phenylenevinylene) (PPV)/n-type polymer structures. ITO/PPV/polyquinoline/Al diodes fabricated under ambient air environment had a turn-on voltage of 3.5 V, luminance levels of over 800 cd/m2, and efficiencies of up to 1 %. Such devices, for example, reversibly switch colors (red -- yellow --green) in the 5-12 V range, facilitating easy pixelation. Origin of the color tunability will be discussed.

14. SUBJECT TERMS
Tunable electroluminescence; light emitting diodes; multicolor electroluminescence; polyquinolines; poly(phenylene vinylene); full color displays; bilayer polymer diodes.

15. NUMBER OF PAGES
2

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

OFFICE OF NAVAL RESEARCH

GRANT NO: N00014-94-1-0540

R&T Code 3132111
Kenneth J. Wynne

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Published

In

POLYMER PREPRINTS

Departments of Chemical Engineering
and Chemistry
University of Rochester, New York 14627

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TUNABLE MULTICOLOR ELECTROLUMINESCENT POLYMER DEVICES FOR FULL COLOR DISPLAYS

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Introduction

Light emitting diodes (LEDs) fabricated from luminescent semiconducting polymers are very promising for a range of display applications and may soon be commercialized.[1] Achievement of color tunability in organic or polymer LEDs is important for multicolor or full color display applications. Various approaches to color tunability in organic and polymer LEDs have been explored, including: blends of electroluminescent conjugated polymers,[2] exploitation of microcavity effects,[3] multilayer stacks of LED structures of various colors,[4] and bilayer heterojunctions of electroluminescent (EL) conjugated polymers.[5] Heterojunctions of EL semiconducting polymers of both a *p-type* (*hole transport*) and an *n-type* (*electron transport*) provide a simple and yet powerful approach to tunable multicolor LEDs that can be easily pixelated for full color displays. Figure 1 shows a schematic illustration of such a multicolor LED structure which is the focus of our paper.

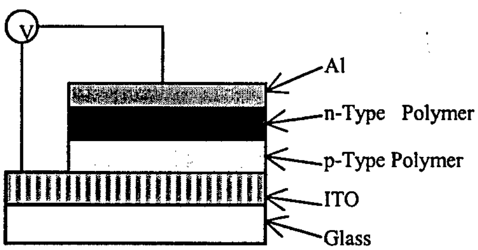

Figure 1. Schematic of tunable multicolor LED structure.

Most of the EL conjugated polymers investigated to date, such as poly(p-phenylene vinylene) (PPV), poly(p-phenylene) (PPP), polythiophenes, polyfluorenes, and their numerous derivatives, are p-type semiconductors. They inject and transport holes more efficiently than electrons. An important exemption are the polyquinolines[5a] and polybenzobisazoles[5b] which are excellent n-type semiconductors[6,7] while also being highly luminescent. These latter classes of EL conjugated polymers (Figure 2) tend to inject and transport electrons more efficiently than holes. Thus by combining both p-type and n-type EL conjugated polymers in bilayer heterojunctions (Figure 1), efficient multicolor emission is in principle possible. However, because of the many possible complications in the photophysics of such polymer/polymer heterojunctions (e.g. exciplex formation,[8] energy transfer, electron transfer, etc.) *multicolor emission* is not an automatic outcome. In fact only a single color emission was observed from most previous bilayer heterojunction LEDs, for example cyano-PPV/PPV,[9] polyquinoxaline/PPV,[10] and polypyridine/PPV among others. We have found that the key to achieving and controlling multicolor emission in polymer/polymer heterojunction LEDs is in controlling the photophysics at the polymer/polymer interface and, very importantly, control of the *finite size effects*.[5,11] The size effects arise from the limited carrier ranges and exciton diffusion lengths in all organic semiconductors.

Experimental

The syntheses and characterizations of the n-type polyquinolines and polybenzobisazoles have previously been reported by our laboratory.[6,7] The sulfonium precursor of PPV in 1 wt% methanol solution was either purchased from Lark Enterprises (Webster, MA) or the same as previously described.[5a] The ITO/PPV/n-type polymer/Al devices (Figure 1) were fabricated and evaluated under ambient laboratory air. The PPV thin films (25-130 nm) were deposited onto ITO-coated glass substrates by spin coating of the sulfonium precursor in methanol solution and followed by thermal conversion in vacuum (~250 °C for 1.5 hr). Thin films (15-100 nm) of an n-type semiconducting polymer from those shown in Figure 2 were spin coated from formic acid solutions onto the PPV layer and dried in vacuum oven overnight. Single layer devices such as ITO/PPV/Al and ITO/n-type polymer/Al were also fabricated in similar ways for comparison purposes. Extensive characterization of all the devices and the bilayer heterojunction films was done in ways similar to previously described procedures.[5,11] In particular, measurements of current (I) – voltage (V), luminance (L) – voltage, EL spectra, and EL microscopy were done in air.

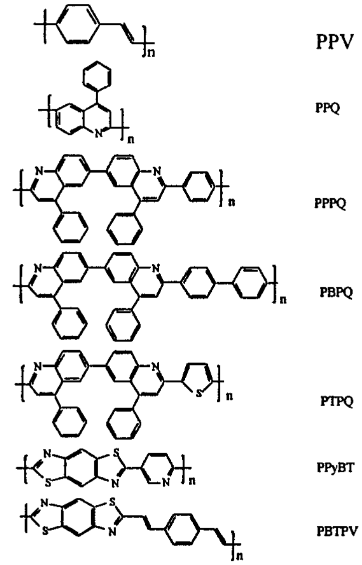

Figure 2. Molecular structures of EL polymers used in multicolor LEDs.

Results and Discussion

Figure 3a shows the EL spectra of a PPQ (67 nm) /PPV (25 nm) bilayer LED. Only orange/red emission from the PPQ layer was observed at all bias voltages from 10-30 V. In this case no emission from the PPV layer is observed and hence the PPV thin film is merely functioning as a hole transport layer for the EL polyquinoline PPQ. On the other hand an LED from a PPQ (33 nm) /PPV (117 nm) gave only green EL emission spectra at all bias voltages from 4.5-30 V (not shown). This means that the polyquinoline thin film is merely functioning as an electron transport layer for the emissive PPV. Shown in Figure 3b are the EL spectra of a PPQ (40 nm) /PPV (25 nm) bilayer LED. Voltage dependent EL spectra are obtained: at low bias voltages (8-10 V) orange/red emission characteristic of the PPQ layer was seen but at higher voltages (~13-20 V or higher) a broad EL band with a more intense green component was observed. Visually, the reversible color switching seen was orange/red ↔ yellow ↔ green as the voltage was varied. These results demonstrate that the emission color from bilayer LED of Figure 1 can be controlled to be a single color from either layer or to be multicolor switchable by voltage depending on the relative layer thicknesses of the polymer/polymer heterojunction.

Similar voltage tunable multicolor LEDs have been fabricated from the n-type semiconducting polymers shown in Figure 2 and others.[5,11] Another interesting example is shown in Figure 4. A PBTPV (50 nm) /PPV (25 nm) LED shows only orange/red electroluminescence at all bias voltages above the turn-on voltage (12 V) (Figure 4a). A PBTPV (15 nm) /PPV (60 nm) LED also showed only a single color (green) at all bias voltages above the turn-on voltage (6 V). In the case of a PBTPV (35 nm) /PPV (25 nm) LED, reversible voltage switchable multicolor was observed (Figure 4b) in which green EL appears first (at low voltages, ~5 V) and eventually changes to orange/red. The visually observed voltage switching of colors was green ↔ yellow ↔ orange/red.

In addition to the novel phenomena of voltage tunability of color in these bilayer heterojunction LEDs, all their performance characteristics (turn-on voltage, EL efficiency, luminance or brightness) were substantially enhanced relative to the corresponding single-layer LEDs. For example, the turn-on voltages of the multicolor LEDs were in the range of 3-5 V compared to 7 V for a single-layer PPV diode and 7-15 V for single-layer n-type polymer devices. Similarly, the EL efficiencies and luminance levels were enhanced by up to two orders of magnitude, reaching ~1% and 800 cd/cm^2 respectively.

Studies of the underlying mechanism of El multicolor switching in these bilayer heterojunction LEDs, including examination of the energetics and barriers at the polymer/polymer interfaces from available HOMO/LUMO levels,[6,7] photophysics and charge transfer processes at the interface, the critical role of film thickness of each polymer in the bilayer heterojunction, and electroluminescence microscopy will be presented and also described in detail elsewhere.

Conclusions

Efficient and bright bilayer heterojunction LEDs constructed from p-type PPV and an n-type polyquinoline or polybenzobisthiazole have been shown to exhibit reversible multicolor emission tunable by the applied bias voltage. Three or more colors can be obtained from such an LED. The simplicity of multicolor pixelation of display systems made from these multicolor LEDs make them attractive for further development and applications.

Acknowledgement. This research was supported by the Office of Naval Research and the National Science Foundation.

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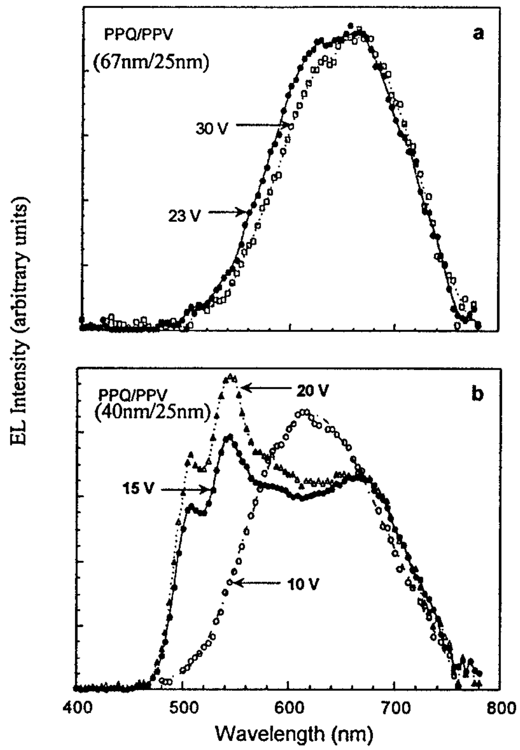

Figure 3. EL spectra of a single-color (a) and multicolor (b) LEDs from PPQ/PPV heterojunctions.

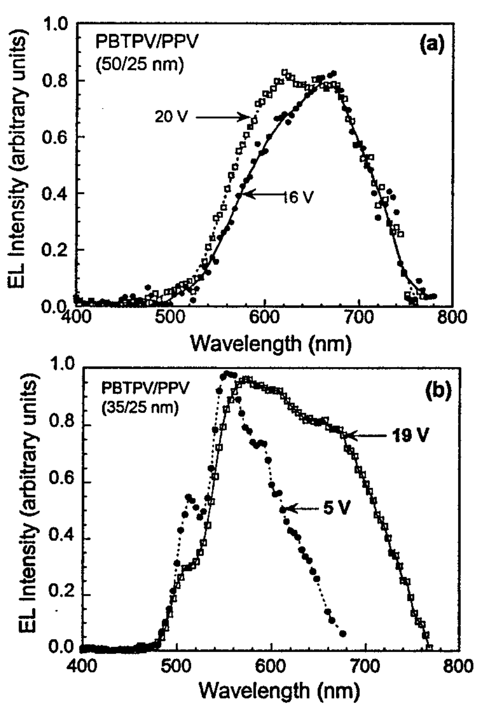

Figure 4. EL spectra of a single-color (a) and multicolor (b) LEDs from PBTPV/PPV heterojunctions.